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CATALYSIS OF CIS-TRANS ISOMERIZATION
BY PARAMAGNETIC SUBSTANCES

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In ~~cis-trans~~ isomerizations about carbon-carbon double bonds are frequently catalyzed by paramagnetic molecules or atoms such as O₂, NO, NO₂, I, Br, Na, K, Rb, Cs.¹ Magoo, Shand, and Eyring² suggested that the low frequency factors³ ($A \sim 10^5$ or less) and low activation energies ($E \sim 10 - 30$ kcal/mole) found for some non-catalyzed isomerizations (e.g., maleic ester \rightarrow fumaric ester) indicate that such isomeric molecules pass through a triplet state when twisting from the cis to the trans form. This idea is illustrated in Fig. 1-a, which gives a schematic representation of the potential energy curves ($V(\theta)$) for the lowest energy singlet (S) and triplet (T) electronic states of an ethylene-type isomer as a function of the angle (θ) of rotation about a carbon-carbon double bond.⁴ Isomerizations via T and S electronic states are indicated by horizontal arrows (1) and (2) in Fig. 1-a, respectively.

The frequency factor for isomerization via path (1) can be related to the energy gap (ϵ in Fig. 1-a)⁵ which results from a mixing of the S and T states by spin-orbit interaction.² For small ϵ 's the frequency factor is approximately proportional to ϵ^2 .⁶ For hydrocarbons,^{2,7} $\epsilon \approx 0.3 - 10 \text{ cm}^{-1}$.

Eyring and Harman⁸ suggested that paramagnetic substances catalyze isomerization through path (1) by providing "a non-homogeneous magnetic field which will act differently on the two magnetic dipoles arising from the spin of the two electrons in the double bond."

Since magnetic spin-spin and "spin of one electron-orbit of another" interactions are weaker than the here already small spin of one electron-orbit of the same electron interactions, it is doubtful that magnetic interactions are responsible for the catalysis of isomerization. The following is a qualitative explanation for the catalytic activity of paramagnetic substances.

If, for example, a doublet electronic state of a catalyst atom interacts with the S and T states of the isomer, two doublet states are formed (D and D' in Fig. 1-b) together with a quartet state. The minimum separation of these doublet states, ϵ' in Fig. 1-b, will in general be determined by the strength of the chemical binding between catalyst and isomer. Since ϵ' need only be of the order of kT to make isomerization by path (1') about $10^4 - 10^7$ times more probable than path (1),⁶ it appears that even weak catalyst-isomer interactions can account for the catalytic effect of paramagnetic molecules. Analogous considerations apply to catalysts in triplet states. No corresponding mechanism exists for catalysis of isomerization by substances in singlet states. These conclusions may represent an improvement over the well-known chemical arguments that some atoms (e.g., iodine) catalyze isomerization by binding to an olefinic molecule and "breaking" the carbon-carbon double bond.

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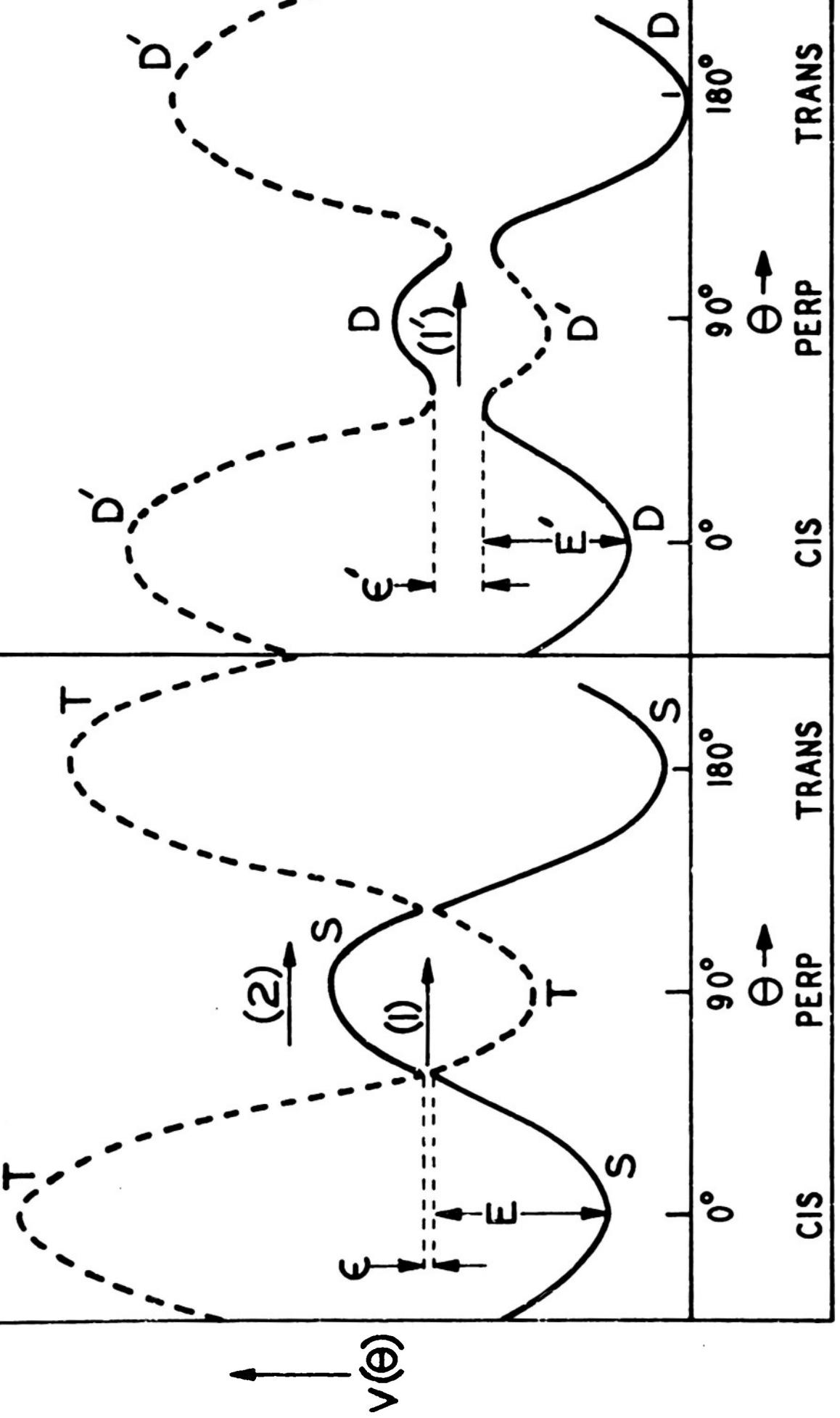
¹ For key references see P. W. Selwood, Chem. Rev., 38, 41 (1946); B. Tamamushi, Bull. Chem. Soc. Japan, 19, 148 (1944); R. G. Dickinson, R. F. Wallis and R. E. Wood, J. Am. Chem. Soc., 71, 1238 (1949).

² J. L. Magee, W. Shand, and H. Eyring, J. Am. Chem. Soc., 63, 677 (1941).

³ Specific isomerization rate (sec^{-1}) = A exp.(-E/RT).

- 4 Compare $V(\theta)$ for ethylene given by R. S. Mulliken and C. C. J. Roothaan, Chem. Rev., 41, 219 (1947).
- 5 The energies ϵ and ϵ' are exaggerated in Fig. 1 for clarity.
- 6 S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill Book Company, New York: 1941, pp. 148-150, 323-328.
- 7 D. S. McClure, J. Chem. Phys., 17, 905 (1949).
- 8 R. A. Harman and H. Eyring, J. Chem. Phys., 10, 557 (1942).

AP-180-1



MOLECULAR COMPOUNDS AND THEIR SPECTRA. III.
THE INTERACTION OF ELECTRON DONORS AND ACCEPTORS

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SOME ERRATA

Page 4, line 4. Substitute: "Lapworth"

Page 5, last line. Add: ", or radicals."

Page 6, line 2. Should read: "between 0 and ω ,"

Page 6, line 8. Should not read "cf.", but: "of"

Page 10, line 19. Should read: "self-explanatory"

Page 18, Remark B4. Should read: "all neutral bases D"

Page 25, Section 9. $H_2O + CO_2$ should be listed under $n + k\pi_d$

Page 27, line 7 in Section 14. Should read: " $b\pi, h\sigma$ and $b\pi, k\sigma$ "

Page 34, line 3 of footnote u. Should read: "Section IV"

Page 34, last line of footnote v. Should read: "Section IV"

Page 36, lines 5-7. Should read everywhere "D" instead of "B"

Page 40, line 23. After "should be polarized", insert "with a large component"

Page 45, line 8. Should read: "u or c"

Page 49, line 1. Should read: " H_2O^+ "

Page 50, next to last line. Should read: " $R^+ + YQ_{n+1}^-$ "

Page 57, first line. Transpose "inner" and "outer"

Page 59, line 11. Should read: "Walker"